

The University of Chicago

A PRECISE
SPECTROPHOTOMETRIC METHOD
FOR THE DETERMINATION OF
IONIZATION CONSTANTS

A DISSERTATION SUBMITTED TO THE
FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1940

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IRVING MYRON KLOTZ

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INTRODUCTION

During the past ten years, much progress has been made toward the perfection of a number of precision methods for the determination of the ionization constants of acids and bases. Largely as a result of the investigations of Harned, MacInnes, von Halban and their collaborators, many refinements have been incorporated into the electromotive force, conductance, and optical methods so that it is now possible to obtain constants with a precision of a few tenths of a per cent.

Perhaps the most widely used of these methods is the one involving the measurement of the potentials of cells without liquid junctions. This method, developed largely by Harned and his collaborators,¹ is a simple and convenient one for weak acids and bases, for with it one may take advantage of the buffer properties of acids and bases and thus obtain relatively accurate measurements even at fairly low hydrogen ion concentrations. Unfortunately the method loses much of its precision for constants of the order² of 10^{-3} and seems to break down completely for values of 10^{-2} or larger.³

A second method is the modern form of conductance measurements which have been carried out primarily in the laboratories of MacInnes and his co-workers.⁴ So far, however, this method has not been applied to dissociations involving divalent ions; and, in common with the electromotive force method, conductance methods lose their precision in very dilute solutions, the region of greatest importance for extrapolation purposes.

The optical method as developed by von Halban and his co-workers⁵ is perhaps the most elegant of all modern methods. By

¹Harned and Owen, Chem. Rev., **25**, 31 (1939).

²Ibid.

³Singleterry, Ph. D. Dissertation, University of Chicago, 1940.

⁴MacInnes and Shedlovsky, J. A. C. S., **54**, 1429 (1932).

⁵Kortum and von Halban, Zeit. f. Phys. Chem., **A170**, 212 (1934).

measuring the relative extinction coefficients of the colored ions involved in acid-base equilibria, these workers have been able to carry their investigations down to concentrations as low as 10^{-6} molar, in which region the precision is still practically the same as in very concentrated solutions. Unfortunately, this method is very limited in applicability; for in most acid-base equilibria of interest, the anion and cation do not show sufficient difference in their absorption of visible and ultraviolet light.

Using these methods investigators have recently collected a vast store of data, particularly on the variation of ionization with temperature. Applying the thermodynamic equation

$$\frac{d \ln K}{dT} = \frac{\Delta H^{\circ}}{RT^2}$$

one may obtain ΔH° , the heat of ionization at infinite dilution. When this step was carried out for the ionization of HSO_4^- ion as determined from electromotive force measurements¹ a value of 2229 cal. mole⁻¹ was obtained for the heat of ionization at 25°C. This value is in startling disagreement with the direct calorimetric value of 5200 cal. mole⁻¹ obtained by Pitzer² while Pitzer's value is in agreement with the heats of dilution data obtained in this laboratory.³ Furthermore, Hamer's value of 91 cal. mole⁻¹ deg.⁻¹ for ΔC_p° at 25°C. cannot be explained by either of the two theoretical approaches⁴ which have been developed recently, for both of them predict a value near 50 cal. mole⁻¹ deg.⁻¹.

The objective of this thesis is to establish a method other than an electromotive force one, with which we may determine the ionization constants of HSO_4^- ion. Since the conductance method of MacInnes and Shedlovsky has not been shown to be valid for divalent electrolytes, and since the optical method of von Halban and Kortum is not applicable to the ionization of HSO_4^- ion, a new method based on some previous observations by J. Mullane⁵ has been devised. This method has made it possible

¹Hamer, J. A. C. S., 56, 860 (1934).

²Pitzer, J. A. C. S., 59, 2365 (1937).

³Gronier, Ph. D. Dissertation, University of Chicago, 1931.

⁴Gurney, J. Chem. Phys., 6, 499 (1938); Everett and Wynne-Jones, Trans. Far. Soc., 35, 1380 (1939).

⁵Mullane, Unpublished Dissertation, University of Chicago.

to adapt spectrophotometric techniques even to acids which do not absorb in the visible or ultraviolet regions of the spectrum. The essential principle of the procedure is to determine the relative effect on the absorption of an acid-base indicator of

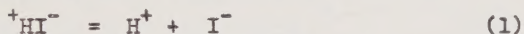
(1) A set of neutral salts, and

(2) The monobasic salt of the acid under consideration.

From the first set of measurements it is possible to correct for salt effects, the apparent changes in hydrogen ion concentration observed in the second set. In contrast to other indicator methods, this one dispenses completely with any necessity of knowing the ionization constant of the indicator, and uses the actual hydrogen ion concentration only as a second order correction in the calculations.

THEORY OF THE METHOD

For an indicator of the type of methyl orange, the equilibrium may be represented by the equation



The corresponding equilibrium constant would be expressed by

$$\frac{(H^+)(I^-)}{({}^+HI^-)} \frac{\gamma_{H^+} \gamma_{I^-}}{\gamma_{{}^+HI^-}} = K \quad (2)$$

or in logarithmic form

$$\log (H^+) + \log [(I^-)/({}^+HI^-)] + \log [\gamma_{H^+} \gamma_{I^-} / \gamma_{{}^+HI^-}] = \log K \quad (3)$$

This equation may be transformed, for convenience, into

$$-\log (H^+) = -\log K + \log [(I^-)/({}^+HI^-)] + \log [\gamma_{H^+} \gamma_{I^-} / \gamma_{{}^+HI^-}] \quad (4)$$

For a given reference solution we may write a similar equation

$$-\log (H^+)_0 = -\log K + \log [(I^-)/({}^+HI^-)]_0 + \log [\gamma_{H^+} \gamma_{I^-} / \gamma_{{}^+HI^-}]_0 \quad (5)$$

Subtracting equation (4) from (5) we obtain

$$\begin{aligned} \log (H^+)/ (H^+)_0 &= \log [(I^-)/({}^+HI^-)]_0 - \log [(I^-)/({}^+HI^-)] \\ &\quad + \log \left[\frac{\gamma_{H^+} \gamma_{I^-}}{\gamma_{{}^+HI^-}} \right] - \log \left[\frac{\gamma_{H^+} \gamma_{I^-}}{\gamma_{{}^+HI^-}} \right]_0 \end{aligned} \quad (6)$$

Let us define

$$\log \left[\gamma_{H^+} \gamma_{I^-} / \gamma_{{}^+HI^-} \right]_0 \equiv \log f \quad (7)$$

Then

$$\log[(H^+)/ (H^+)_0] + \log(f/f_0) = \log[(I^-)/(^+HI^-)]_0 - \log[(I^-)/(^+HI^-)] \quad (8)$$

The effect of the addition of neutral salts is merely to change the activity coefficients of the indicator and of the hydrogen ion. Any change in hydrogen ion concentration due to increased dissociation of the indicator is negligible, since the original acid concentration is about one hundred times the indicator concentration. Therefore, for the addition of neutral salts

$$\log[(H^+)/ (H^+)_0] = 0 \quad (9)$$

$$\log(f/f_0) = \log[(I^-)/(^+HI^-)]_0 - \log[(I^-)/(^+HI^-)] \quad (10)$$

When the salt of a "weak" acid and strong base, (such as Na_2SO_4) is added, however, the removal of hydrogen ion has a pronounced effect on $\log(H^+)$ so that we must retain the full equation (primes used to distinguish the equation from that given for neutral salts)

$$\log[(H^+)'/ (H^+)_0] + \log(f'/f_0) = \log[(I^-)/(^+HI^-)]_0 - \log[(I^-)/(^+HI^-)]' \quad (11)$$

It is necessary, then, to obtain $\log[(I^-)/(^+HI^-)]$ for the indicator solution containing no salt, and containing various amounts and kinds of salts, respectively. To do this we make use of Beer's Law in its logarithmic form:

$$\log(I_0/I) = kcd \quad (12)$$

where I_0 = intensity of incident light
 I = intensity of transmitted light
 k = extinction coefficient of the absorbing substance
 c = concentration of the absorbing substance
 d = length of the absorption cell

When we have the indicator of total concentration, c , in basic solution

$$\log(I_0/I)_b = k_b cd \quad (13)$$

whereas in strong acid solution in which the indicator is completely in the acid form

$$\log(I_0/I)_a = k_a cd \quad (14)$$

If we define $k' = kd$

$$k'_b = \frac{1}{c} \log(I_0/I)_b \quad (15)$$

$$k'_a = \frac{1}{c} \log(I_0/I)_a \quad (16)$$

In any solution of intermediate acidity where the degree of dissociation is α

$$\log (I_o/I)_x = \alpha c k'_b + (1-\alpha)ck'_a \quad (17)$$

Solving for α we obtain

$$\alpha = \frac{\log (I_o/I)_x - \log (I_o/I)_a}{\log (I_o/I)_b - \log (I_o/I)_a} \quad (18)$$

so that $\alpha/1-\alpha$, which is equal to $(I^-)/(^+HI^-)$ is given by

$$\frac{(I^-)}{(^+HI^-)} = - \frac{\log (I_o/I)_x - \log (I_o/I)_a}{\log (I_o/I)_x - \log (I_o/I)_b} \quad (19)$$

Since we use a reference indicator solution instead of pure solvent

$$\frac{(I^-)}{(^+HI^-)} = - \frac{\log \left(\frac{I_r I_o}{I I_r} \right)_x - \log \left(\frac{I_r I_o}{I I_r} \right)_a}{\log \left(\frac{I_r I_o}{I I_r} \right)_x - \log \left(\frac{I_r I_o}{I I_r} \right)_b} \quad (20)$$

$$= - \frac{\log (I_r/I)_x - \log (I_r/I)_a}{\log (I_r/I)_x - \log (I_r/I)_b} \quad (20a)$$

(20a) follows from (20) because (I_o/I_r) is a constant even if the respective intensities change over a period of time. Let us define

$$- \frac{\log (I_r/I)_x - \log (I_r/I)_a}{\log (I_r/I)_x - \log (I_r/I)_b} = R = \frac{(I^-)}{(^+HI^-)} \quad (21)$$

Substituting in equations (10) and (11) we obtain for the addition of neutral salt

$$\log(f/f_o) = \log R_o - \log R \quad (22)$$

and for the salt of a weak acid and a strong base

$$\log (H^+) / (H^+)_o + \log (f'/f_o) = \log R_o - \log R' \quad (23)$$

Three experimental quantities, $(I_r/I)_x$, $(I_r/I)_b$, and $(I_r/I)_a$ are necessary for the evaluation of R . No difficulties are encountered in the determination of the first two, but because of the nature of the indicator a special procedure is necessary to evaluate $(I_r/I)_a$ for methyl orange.

The difficulty arises because this indicator is a relatively strong acid, having an ionization constant of 4×10^{-4} .

Hence it is necessary to have a very concentrated acid solution to convert the indicator completely into its acid form. It is impossible to obtain the necessary hydrogen ion concentration by the simple addition of acid without the introduction of two undesirable effects. In the first place, the increase in volume due to the addition of a large quantity of concentrated HCl would remove so much indicator from the optical path that it would be difficult to make a suitable correction. Secondly, the increased ionic strength would exert an appreciable effect upon the absorption coefficient of the acid form of the indicator.¹ To obviate these difficulties the following technique was adopted.

Small quantities of concentrated HCl were added successively to the working cell and the respective transmissions measured (see Table 1). Since the quantities of added acid were small, salt effects on the transmission of the acid form were negligible.² To determine the correction for the removal of indicator from the optical path a small quantity of distilled water was added to the working cell and the effect on the transmission observed (see footnote to Table 1). It was then assumed that concentrated HCl behaves exactly as pure water as far as dilution effects are concerned. This change in transmission, expressed as the change in $\log(I_r/I)$ per cc. diluant, was used, therefore, as the basis for the correction of the transmission of the respective acid solutions for dilution. These corrected transmissions were plotted against the reciprocal of the acid concentration and extrapolated to infinite hydrogen ion concentration (Figure 1). The intercept was taken as $\log(I_r/I)_a$.

TABLE 1 - DETERMINATION OF $\log(I_r/I)_a$ FOR NaCl AT 24.9°C.

Cc. Acid	Log (I/I_r) Observed	Dilution Correction* Including That Due to Addition of 0.5 cc. NaOH	Log (I/I_r) Corrected	1
				Cc. Acid
0.4	-.2263	-.0019	-.2282	2.5
0.8	-.2326	-.0029	-.2355	1.25
1.2	-.2338	-.0038	-.2376	0.83

* $\Delta\log(I/I_r) = -.0022$ per cc. of water added.

¹Sidgwick, Worboys, and Woodward, Proc. Roy. Soc., 129, 537 (1930).

²Ibid.

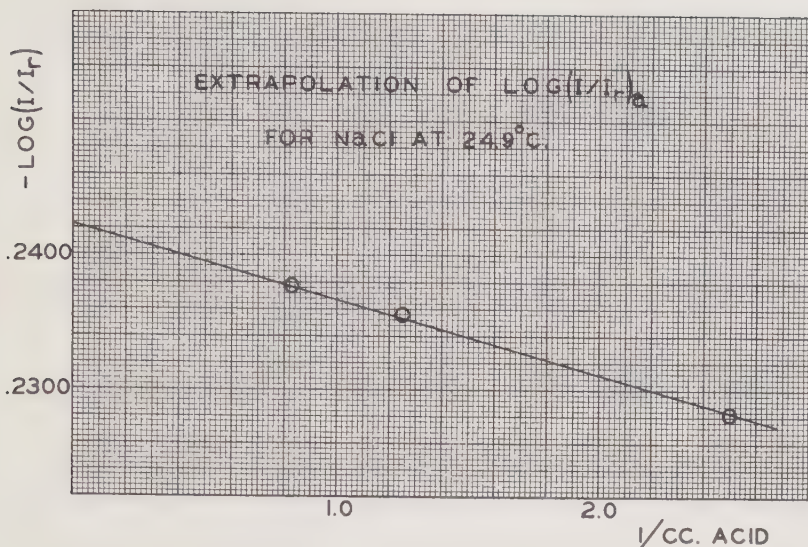


Figure 1

A similar procedure is unnecessary for the determination of $\log(I_r/I)_0$ because a few drops of 1N NaOH are sufficient to convert the indicator to more than 99.99% basic form.

We have to calculate yet the ionization constant of the weak acid HA from the change in H^+ concentration due to the addition of the salt NaA or KA to the indicator solution. In actual practice it has proved to be convenient to distinguish between the following two cases:



but the following equations which are developed for the specific case of $SO_4^{=}$ are also valid for an ion of the type $A^{=}$.

If we subtract equation (22) from (23) we obtain

$$\log[(H^+)'/(H^+)_0] + \log(f'/f_0) - \log(f/f_0) = \log R - \log R' \quad (26)$$

We shall assume that

$$\log(f'/f_0) = \log(f/f_0) \quad (27)$$

for a given ionic strength. This is certainly not true for any finite concentration. However, as we go to more and more dilute solutions, equation (27) becomes a better and better approxima-

tion, and for various chlorides is valid within experimental error for concentrations below 0.01 molar (Figure 3). Equations (26) and (27) reduce to

$$\log[(H^+)'/(H^+)_0] = \log R - \log R' \stackrel{=}{=} \log S \quad (28)$$

$$\log[(H^+)'/(H^+)_0] = \log S \quad (29)$$

$$(H^+)' = (H^+)_0 S \quad (30)$$

The constant for the equilibrium expressed by (25) is

$$\frac{(H^+)'(SO_4^{=})}{(HSO_4^-)} \frac{\gamma_{H^+} \gamma_{SO_4^{=}}}{\gamma_{HSO_4^-}} = K \quad (31)$$

It is obvious that the following relations are true.

$$(H^+)' = (H^+)_0 S$$

$$(HSO_4^-) = (H^+)_0 - (H^+)' = (H^+)_0 (1-S) \quad (32)$$

$$(SO_4^{=}) = m_{Ia_2SO_4} - m_{HSO_4^-} = m - (H^+)_0 (1-S)$$

Substituting in equation (32) we obtain

$$\frac{(H^+)_0 S [m - (H^+)_0 (1-S)]}{(H^+)_0 (1-S)} \frac{\gamma_{H^+} \gamma_{SO_4^{=}}}{\gamma_{HSO_4^-}} = K \quad (33)$$

$$\frac{S [m - (H^+)_0 (1-S)]}{(1-S)} \frac{\gamma_{H^+} \gamma_{SO_4^{=}}}{\gamma_{HSO_4^-}} = K = K' \frac{\gamma_{H^+} \gamma_{SO_4^{=}}}{\gamma_{HSO_4^-}} \quad (34)$$

Thus we see that our final expression does not contain the indicator constant, and contains $(H^+)_0$ only as part of a small correction in the sulfate ion concentration.

To obtain K we must now resort to one of the following three procedures.

1. Plot K' against $\sqrt{\mu}$, μ being the ionic strength, and extrapolate to $\sqrt{\mu} = 0$.
2. Obtain values of $\frac{\gamma_{H^+} \gamma_{SO_4^{=}}}{\gamma_{HSO_4^-}}$ by the use of the Debye-Huckel Limiting Law

$$\log (\gamma_{H^+} \gamma_{SO_4^{=}} / \gamma_{HSO_4^-}) = - 4 A \sqrt{\mu} \quad (35)$$

where A is a constant for a given temperature and solvent and equal to -0.509 for water at 25°C.

Plot K against μ and extrapolate to $\mu = 0$.

3. Obtain values for $\gamma_{H^+} \gamma_{SO_4^{2-}} / \gamma_{HSO_4^-}$ by means of the completed form of the Debye-Hückel equation

$$\log \frac{\gamma_{H^+} \gamma_{SO_4^{2-}}}{\gamma_{HSO_4^-}} = - \frac{4 A \sqrt{\mu}}{1 + a \sqrt{\mu}} \quad (36)$$

In this equation a is a parameter which is a function of the respective distances of closest approach of the ions. For this work a was determined empirically by successive substitutions until a straight, practically horizontal line was obtained in a plot of K against μ . (A similar procedure has been used by Naidich and Ricci.¹) This line is then extrapolated to $\mu = 0$ (see Figures 5 and 6).

All three procedures should give the same result. In practice, however, the first and second methods are difficult to use because much weight must be given to points in the very dilute range, the region of decreasing precision. The third method, however, involves a straight line extrapolation and therefore gives the most precise results.

APPARATUS AND MATERIALS

The problem requires the construction of a spectrophotometer which can detect very small changes in absorption but which need not have a rapid response. A D.C. amplifier was constructed which with methyl orange as an indicator could detect salt effects equivalent to a change in $\log(H^+)$ of 0.001-0.002 unit. For this precision to be significant it is also necessary to have a very stable light source and to thermostat the absorption cells.

A. The Light Source

For some preliminary work, a Mazda lamp #1183, taking seven amperes at six volts, was tried. At first, power was supplied by a small generator operated by a synchronous motor and "floated" across one six volt storage battery. The fluctuations, while too fast to be detected by an electrometer, were very troublesome with a vacuum tube amplifier. An improvement was ob-

¹Naidich and Ricci, J. A. C. S., 61, 3268 (1939).

served when the large, laboratory D.C. generator was used with most of the power being dissipated through a water-cooled resistor, and with a second storage battery "floated" across the line. This method gave values of I_0 whose average variation was around 0.3% in any given set of readings. The variations throughout a complete day were much larger, however, and were rather sensitive to changes in the total load being carried by the generator.

The light source finally adopted consisted of a straight single-filament Mazda lamp, rated by the manufacturer at 3.5-4.0 volts and 0.5 of an ampere. Two high capacity, six volt storage batteries (Willard 119-6) connected in parallel, served as the power supply. The voltage drop across the lamp was adjusted to 3.8 volts by means of a rheostat in series with the lamp so that a life of over 300 hours might be assured. To minimize fluctuations due to air currents, the lamp was mounted in a ventilated metal can, and after a warming-up period of an hour, very steady readings were obtained. In any set of readings, the average variation in intensity was usually less than 0.1% and since this was usually due to a uniform drift, the effect on the ratio, I/I_0 , was much less. The variation throughout a day was often as high as 4-5% but could have been kept lower, had it been necessary, by the use of a felt-lined box to protect the batteries from temperature fluctuations in the room.

B. The Air Thermostat

An air thermostat was constructed to contain the absorption cells during a set of measurements. On an angle iron framework and galvanized iron base, three sheets of one-half inch Celotex were placed. Two coats of aluminum paint were then applied and the inside and outside were covered with aluminum foil. To enable manipulations to be carried out on the absorption cells within the thermostat, a sloping panel was constructed at the top. This panel contained a window and two trap door openings with rubber sleeves attached so that the experimenter could insert his arms and observe his manipulations without fear of air and heat leakage. Water passing through a set of copper coils and a radiator taken from an automobile heater served as the cooling elements while a resistor capable of dissipating 200 watts was used for heating. The temperature was controlled by a mercury regulator connected to a thermionic tube relay system. When clean

mercury was used the temperature regulation was within 0.03°C . at any one position. Because of differences in temperature at different points in the thermostat it was important to keep the cells at one fixed position between readings.

It was also found necessary to use a small, hand-type vacuum cleaner fan to produce adequate stirring of the air within the thermostat. The fan was mounted on an iron stand independent of the table carrying the thermostat and spectrograph so that vibrations could not be transmitted to the optical system.

Double glass windows were used to avoid condensation of moisture upon the glass in the optical path when low temperatures were maintained. Provision was also made for blowing dry air against the outside windows of the thermostat but in practice this proved to be unnecessary. To avoid condensation of moisture on the absorption cells, a stream of dry air was passed slowly into the thermostat whenever temperatures below that of the room were used.

C. The Absorption Cells

The reference cell, which contained merely the standard indicator solution, had been accurately ground and polished to a length of about 5 cm. and had a diameter of about 3 cm. The cell was encased in a brass tube with threaded brass caps to exert the mechanical pressure necessary to hold the windows. The working cell, which contained the indicator solution to which the various salts were added, was also about 5 cm. long, but the glass tube of this cell was only 2 cm. in diameter. Pyrex windows were fused to the ends of the tube. At the center of the tube was a neck, 1 cm. in diameter, to which a 200 cc. pyrex flask had been sealed. The volume of this flask made it possible to use an ordinary analytical balance for weighing out amounts of salt corresponding to concentrations as low as 0.0005 moles per liter. The working cell was also encased in a brass tube but mechanical pressure to hold the windows was unnecessary. A set of pins in the carriage fitted corresponding holes in the brass tubes and thereby held the cells firmly in position.

D. The Monochromator

A Steinheil spectrograph (#5062) was used to obtain the desired monochromation. The approximate settings, as specified

by the manufacturer, were made first, but the final adjustments were made with the aid of the lines of a mercury or sodium arc focused upon a ground glass plate inserted in the camera arm. In general, the wave length chosen for measurement was near the peak of the absorption band of the highly absorbing form of the indicator but sufficiently far from the maximum so that the absorption of the other form of the indicator was small. The slit in front of the photocell was set to cut off a band from 5 to 20 Å. in width, the exact value depending on the indicator, concentration of the indicator, and the temperature. For a given indicator, the same band was used throughout all of the measurements.

E. The Photocell and Amplifier

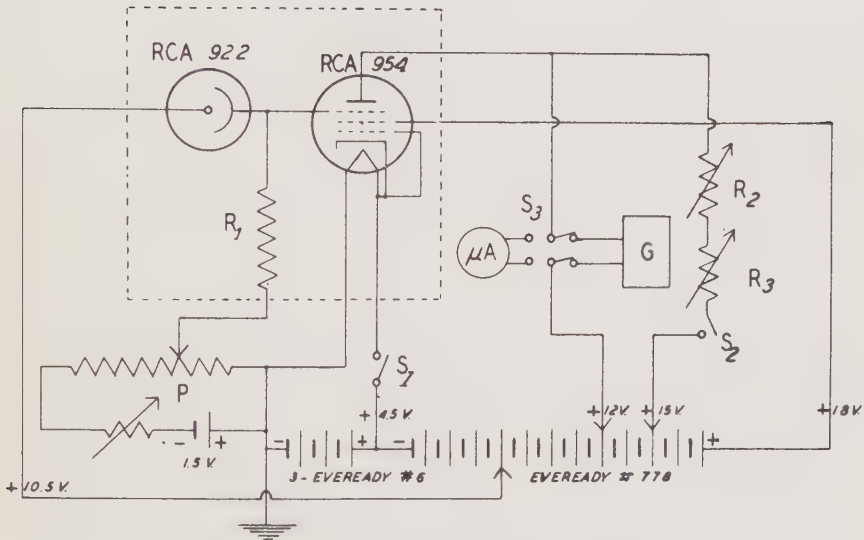
Much trouble was encountered in obtaining a photocell suitable for use with a 10^{10} ohm resistor in the amplifier. The problem of "polarization" drifts has recently been analyzed very thoroughly¹ and special cells have been designed which eliminate these drifts completely. Unfortunately, such cells were not available for this work. However, it was found possible to reduce these drifts to a negligible value by taking a number of precautions with a specially selected RCA 922 CsO vacuum-type photocell. This cell, having a dark resistance greater than 10^{12} ohms, was carefully washed, and fitted with a thin copper, external guard ring. When operated at 10 1/2 volts and exposed only to low light intensities, this cell showed only very minute "polarization" drifts.

The photocurrents were amplified by an RCA 954 vacuum tube in a circuit similar to that of Gabus and Pool.² The actual circuit (Figure 2) differs somewhat from that used by these workers. In the first place a potentiometer was introduced into the grid circuit so that the amplifier could be adapted to null measurements. Secondly, the voltage on the balancing circuit was reduced slightly to permit the use of wire-wound rheostats. Finally, the voltage on the photocell was decreased to 10 1/2 volts in order to reduce "polarization" drifts.

¹Boutry and Gillod, Phil. Mag., **28**, 163 (1939).

²Gabus and Pool, Rev. Sci. Instr., **8**, 196 (1937).

PHOTOCELL AND AMPLIFIER



P = LEEDS AND NORTHRUP STUDENT TYPE POTENTIOMETER

G = GALVANOMETER

μA = MICROAMMETER

R_1 = 10^{10} OHM S. S. WHITE RESISTOR

R_2 = 50000 OHM RHEOSTAT

R_3 = 1000 OHM RHEOSTAT

DOTTED LINE INDICATES BOX WHICH WAS ATTACHED
TO CAMERA ARM OF SPECTROGRAPH

Figure 2

F. Materials

NaCl (Baker's Analyzed, Fused) was recrystallized once from a clear, distilled water solution by addition of 95% alcohol, and was then dried in an oven at 120°C.

KCl (Mallinckrodt's Analytical Reagent) was recrystallized once from distilled water and dried at 120°C.

BaCl₂·2H₂O (Mallinckrodt's Analytical Reagent) was recrystallized once from distilled water, and was dehydrated and dried at 120°C.

KNO₃ (Baker's Reagent) was recrystallized once from distilled water and dried at 120°C.

Na₂SO₄ (Kahlbaum's, Fused) was recrystallized twice from distilled water as the decahydrate and allowed to remain in a dessicator until needed. Several months later the white crystalline powder was heated in an oven at 120°C.

K₂SO₄ (De Haen's) was recrystallized once from distilled water and dried at 120°C.

Na(ClCH₂CO₂) was prepared from the corresponding acid. Chloroacetic acid (Baker's Analyzed) was distilled twice under reduced pressure. The fraction finally taken melted from 62.4-62.6°C. It was dissolved in 95% alcohol and an alcoholic NaOH solution added until phenolphthalein paper gave a slight pink color. A small portion of chloroacetic acid was then used for back titration. The precipitated salt was washed with 95% ethyl alcohol and 99% isopropyl alcohol, respectively, and dried over CaCl₂. Before the salt was weighed out it was also dried under vacuum for four days.

HCl was prepared by distillation of a mixture of commercial HCl and water in an all glass still. Commercial HCl was used in the early part of the work (some of the measurements at 15° and 25°) but was found to cause destruction of the indicator at higher temperatures.

Methyl orange (Grübler and Co.) was recrystallized once from water and dried over CaCl₂. Stock solutions were made by the addition of approximately five mg. of indicator to four liters of distilled water. The solution was acidified with five or six drops of distilled HCl.

PROCEDURE

Prior to a series of measurements both the reference cell and working cell were rinsed four or five times with stock indicator solution. The working cell was then allowed to drain for about half an hour, and was filled with 200 cc. of indicator solution carefully measured with a calibrated pipette. Approximately 50 cc. of the same solution was added to the reference cell. Both cells were placed in the thermostat and allowed to remain for about twelve hours before any optical observations were made.

From two to twelve hours before measurements were started dry salts were weighed into small tubes each provided with a ground glass stopper. As soon as the weighings were completed, the tubes also were placed in the thermostat.

The light source and amplifier were turned on (i.e. switches S_1 and S_2 closed, S_3 turned toward microammeter) about an hour before observations were begun. In the meantime the temperature of the working cell was determined by means of a thermometer inserted directly into the cell. The thermometer was calibrated against a U. S. Bureau of Standards mercury thermometer.

When the amplifier became sufficiently steady, as indicated by galvanometer zero point readings, optical measurements were begun. For each measurement the following operations were carried out. With the potentiometer, P, reading zero and switch, S_3 , thrown toward the microammeter, rheostat R_2 was adjusted to make the reading of the ammeter zero. S_3 was then changed to substitute the galvanometer for the microammeter and rheostat R_3 manipulated to obtain a finer zero adjustment. S_3 was then turned back to the microammeter side, the shutter of the spectrograph was opened and light allowed to fall on the photocell. The reading of the microammeter, and then of the galvanometer, was decreased to zero by increasing the potential drop in the grid circuit by means of the potentiometer P. The potentiometer had been calibrated against a type K potentiometer which in turn had been calibrated by the method of Young and Hartsuch.¹ The potential drop required to bring the plate current back to zero was taken

¹Hartsuch, Ph. D. Dissertation, University of Chicago, 1935.

as the measure of the intensity of the light incident on the photocell.

All intensity measurements were made in this manner. First the ratio of the light transmitted by the two cells, with salt added to neither, was determined. Then the contents of a weighing tube were added to the working cell, and the cell inverted from ten to thirty times to insure complete homogeneity. To minimize heat transfer from the hands during the mixing process, a layer of felt was used. Even with such precautions, however, the temperature of the working cell changed by 0.1-0.2 of a degree, so that thirty to sixty minutes were allowed between each salt addition and the corresponding transmission measurement.

To determine the absorption of the basic form, 0.5 cc. of 1N NaOH was added. To obtain the relative absorption of the acid form, successive portions of concentrated HCl were added and the readings were extrapolated as explained in the section on the theory of the method.

EXPERIMENTAL RESULTS

Table 2 and Figures 3 and 4 show the effects of various salts on methyl orange. In a number of cases, the ionic strengths (i.e. the HCl concentration) of the solutions in the reference cells differ by small amounts. Since for purposes of comparison it is convenient to have reference points of the same ionic strength, short graphical extrapolations to a common reference point were made and the difference in $\log (R_0/R)$ between the experimental and common reference points added to each set of data respectively. These "corrected" values of $\log (R_0/R)$ are indicated in the final column of Table 2.

The values of KHSO_4^- and $\text{KClCH}_2\text{COOH}$ calculated by the methods indicated in an earlier section are shown in Tables 3 and 4 and in Figures 5 and 6.

DISCUSSION

A. Sources of Possible Error

From the internal consistency of the points of any given curve, and from the reproducibility obtained in cases where duplicate determinations were made, the precision of the method seems to be about 0.001 pH unit, i.e. 0.2% in hydrogen ion concentration. Conclusions concerning the accuracy, however, must

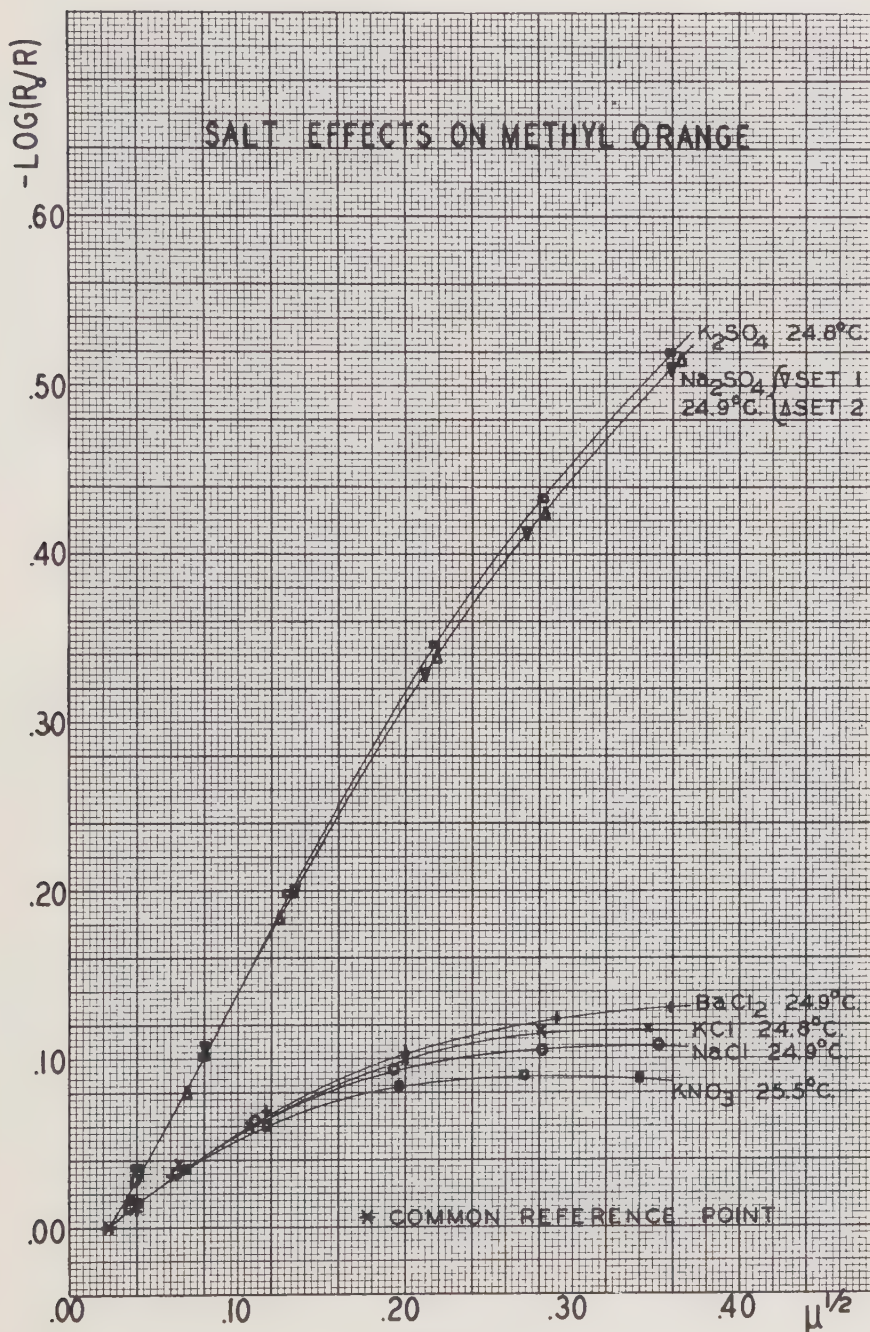


Figure 3

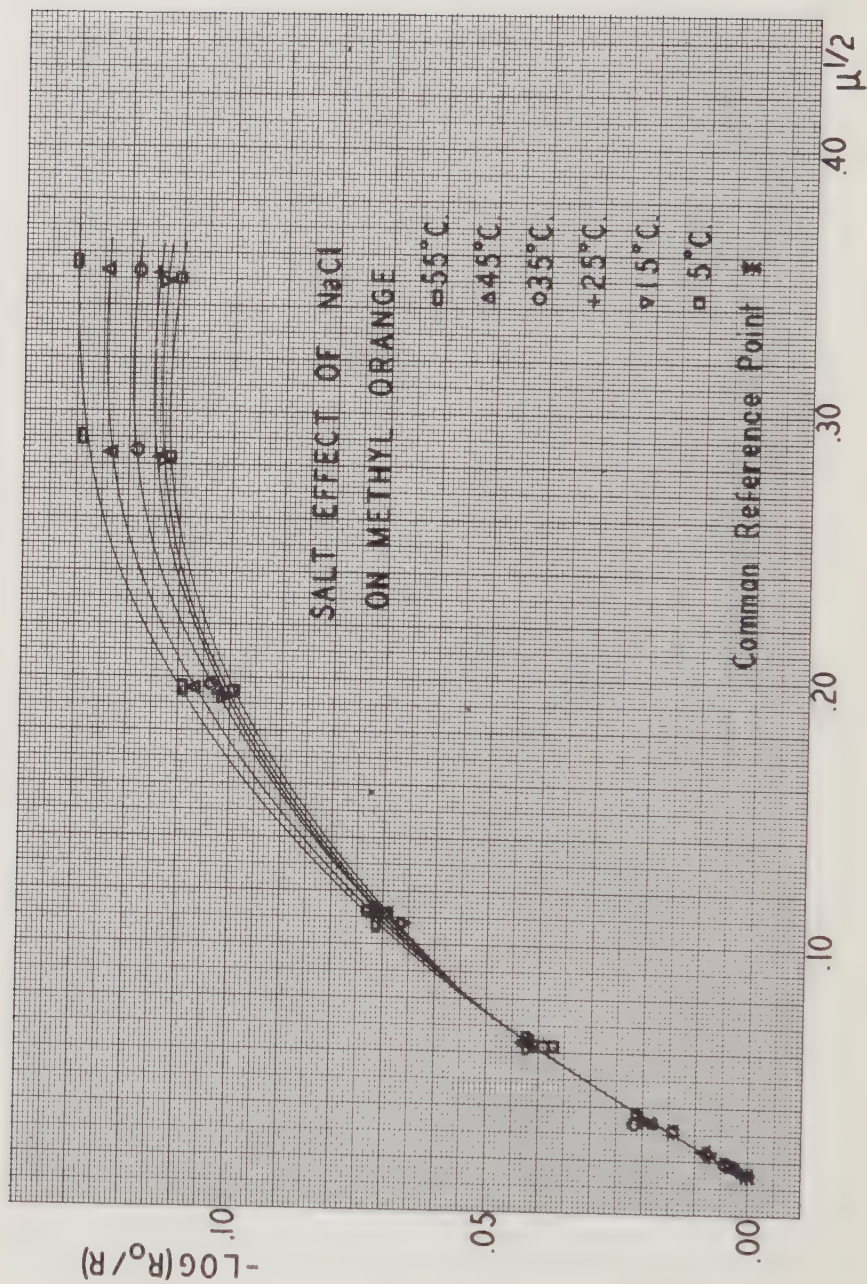


Figure 4

TABLE 2 - SALT EFFECTS ON METHYL ORANGE

Solution	Molality of Salt	Log(I/I _r)	$\mu^{1/2}$	Log(R _o /R)	Log(R _o /R) Refer. Pt. $\mu^{1/2} = .0150$
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KCl at 24.8°C.

 $\lambda = 5200\text{\AA}.$

Acid form		-.2349			
Base form		.2885			
Stock solution		.0088	.0235	.0000	
Salt solution(1)	.00087	.0130	.0377	-.0142	
" " (2)	.00375	.0205	.0656	-.0391	
" " (3)	.01099	.0273	.1074	-.0617	
" " (4)	.03913	.0387	.1992	-.0994	
" " (5)	.07889	.0436	.2818	-.1158	
" " (6)	.11979	.0439	.3469	-.1169	

BaCl₂ at 24.9°C. $\lambda = 5200\text{\AA}.$

Acid form		-.2393			
Base form		.2867			
Stock solution		.0066	.0235	.0000	-.0078
Salt solution(1)	.00032	.0105	.0387	-.0132	-.0210
" " (2)	.00112	.0166	.0626	-.0329	-.0407
" " (3)	.00442	.0276	.1175	-.0693	-.0771
" " (4)	.01320	.0376	.2004	-.1022	-.1100
" " (5)	.02774	.0443	.2894	-.1247	-.1325
" " (6)	.04231	.0459	.3570	-.1300	-.1378

KNO₃ at 25.5°C. $\lambda = 5200\text{\AA}.$

Acid form		-.4340			*
Base form		.3886			
Stock solution		-.0085	.0192	.0000	.0037
Salt solution(1)	.00129	.0003	.0407	-.0186	-.0149
" " (2)	.00442	.0097	.0692	-.0388	-.0351
" " (3)	.01304	.0214	.1158	-.0636	-.0599
" " (4)	.03792	.0328	.1957	-.0881	-.0844
" " (5)	.07347	.0358	.2717	-.0944	-.0907
" " (6)	.11590	.0346	.3410	-.0921	-.0884

*Refer. pt. $\mu^{1/2} = .0235$

TABLE 2 - Continued

Solution	Molality of Salt	$\text{Log}(I/I_r)$	$\mu^{1/2}$	$\text{Log}(R_o/R)$	$\text{Log}(R_o/R)$ Refer. Pt. $\mu^{1/2} = .0150$
Na_2SO_4 at 24.9°C . Set #1 $\lambda = 5200\text{\AA}$.					
Acid form		-.2383			
Base form		.2877			
Stock solution		.0079	.0235	.0000	
Salt solution(1)	.00045	.0174	.0435	-.0314	
" " (2)	.00209	.0408	.0826	-.1086	
" " (3)	.00578	.0679	.1338	-.1995	
" " (4)	.01480	.1047	.2120	-.3285	
" " (5)	.02479	.1276	.2737	-.4144	
" " (6)	.04259	.1510	.3582	-.5100	
Na_2SO_4 at 24.9°C . Set #2 $\lambda = 5200\text{\AA}$.					
Acid form		-.2390			
Base form		.2870			
Stock solution		.0069	.0235	.0000	
Salt solution(1)	.00039	.0157	.0416	-.0292	
" " (2)	.00150	.0313	.0711	-.0806	
" " (3)	.00517	.0622	.1267	-.1836	
" " (4)	.01583	.1064	.2192	-.3380	
" " (5)	.02660	.1296	.2835	-.4261	
" " (6)	.04438	.1517	.3656	-.5171	
K_2SO_4 at 24.8°C . $\lambda = 5200\text{\AA}$.					
Acid form		-.2358			
Base form		.2893			
Stock solution		.0082	.0235	.0000	
Salt solution(1)	.00043	.0194	.0430	-.0369	
" " (2)	.00198	.0394	.0806	-.1033	
" " (3)	.00558	.0680	.1315	-.1992	
" " (4)	.01573	.1097	.2185	-.3457	
" " (5)	.02619	.1326	.2813	-.4328	
" " (6)	.04277	.1537	.3589	-.5198	

TABLE 2 - Continued

Solution	Molality of Salt	$\text{Log}(I/I_r)$	$\mu^{1/2}$	$\text{Log}(R_o/R)$	$\text{Log}(R_o/R)$ Refer. Pt. $\mu^{1/2} = .0150$
$\text{ClCH}_2\text{CO}_2\text{Na}$ at 24.8°C . $\lambda = 5200\text{\AA}$.					
Acid form		-.4330			
Base form		.3900			
Stock solution		-.0129	.0192	.0000	-.0037
Salt solution(1)	.00071	.0683	.0329	-.1743	-.1780
" " (2)	.00346	.2097	.0619	-.5336	-.5373
" " (3)	.00808	.2874	.0919	-.8282	-.8319
" " (4)	.01497	.3267	.1239	-1.0609	-1.0646
" " (5)	.02171	.3437	.1486	-1.2065	-1.2102
NaCl at 4.7°C . $\lambda = 5200\text{\AA}$.					
Acid form		-.3325			
Base form		.5623			
Stock solution		.0100	.0187	.0000	-.0035
Salt solution(1)	.00064	.0154	.0315	-.0111	-.0146
" " (2)	.00354	.0265	.0624	-.0337	-.0372
" " (3)	.01215	.0425	.1118	-.0661	-.0696
" " (4)	.03749	.0576	.1945	-.0958	-.0993
" " (5)	.08003	.0641	.2825	-.1085	-.1120
" " (6)	.12202	.0632	.3498	-.1069	-.1104
NaCl at 15.1°C . $\lambda = 5200\text{\AA}$.					
Acid form		-.2159			
Base form		.3317			
Stock solution		.0058	.0235	.0000	-.0078
Salt solution(1)	.00065	.0095	.0346	-.0122	-.0200
" " (2)	.00327	.0163	.0618	-.0344	-.0422
" " (3)	.01112	.0235	.1080	-.0582	-.0660
" " (4)	.03646	.0347	.1924	-.0936	-.1014
" " (5)	.07880	.0383	.2817	-.1050	-.1128
" " (6)	.12103	.0384	.3487	-.1054	-.1132

TABLE 2 - Continued

Solution	Molality of Salt	$\text{Log}(I/I_r)$	$\mu^{1/2}$	$\text{Log}(R_o/R)$	$\text{Log}(R_o/R)$ Refer. Pt. $\mu^{1/2} = .0150$
NaCl at 24.9°C. $\lambda = 5200\text{\AA}.$					
Acid form		-.2417			
Base form		.2870			
Stock solution		.0074	.0235	.0000	-.0078
Salt solution(1)	.00076	.0112	.0362	-.0125	-.0203
" " (2)	.00353	.0175	.0639	-.0333	-.0411
" " (3)	.01186	.0268	.1114	-.0638	-.0716
" " (4)	.03684	.0361	.1934	-.0940	-.1018
" " (5)	.07974	.0394	.2824	-.1051	-.1129
" " (6)	.12319	.0398	.3518	-.1066	-.1149
NaCl at 34.9°C. $\lambda = 5200\text{\AA}.$					
Acid form		-.3847			
Base form		.3140			
Stock solution		.0069	.0184	.0000	-.0036
Salt solution(1)	.00083	.0139	.0342	-.0177	-.0213
" " (2)	.00353	.0208	.0622	-.0353	-.0389
" " (3)	.01229	.0338	.1123	-.0689	-.0725
" " (4)	.03845	.0457	.1970	-.0997	-.1033
" " (5)	.08103	.0513	.2853	-.1146	-.1182
" " (6)	.12411	.0513	.3528	-.1146	-.1182
NaCl at 44.4°C. $\lambda = 5200\text{\AA}.$					
Acid form		-.4010			
Base form		.2757			
Stock solution		.0104	.0185	.0000	-.0036
Salt solution(1)	.00083	.0161	.0342	-.0157	-.0193
" " (2)	.00372	.0248	.0637	-.0394	-.0430
" " (3)	.01226	.0352	.1123	-.0683	-.0719
" " (4)	.03808	.0475	.1960	-.1031	-.1067
" " (5)	.08110	.0532	.2844	-.1195	-.1231
" " (6)	.12421	.0535	.3529	-.1204	-.1240
NaCl at 54.6°C. $\lambda = 5200\text{\AA}.$					
Acid form		-.5190			
Base form		.4204			
Stock solution		.0073	.0187	.0000	-.0037
Salt solution(1)	.00106	.0166	.0376	-.0173	-.0210
" " (2)	.00382	.0276	.0646	-.0384	-.0421
" " (3)	.01123	.0429	.1076	-.0674	-.0711
" " (4)	.03810	.0623	.1961	-.1054	-.1091
" " (5)	.08369	.0725	.2899	-.1253	-.1290
" " (6)	.12661	.0732	.3563	-.1265	-.1302

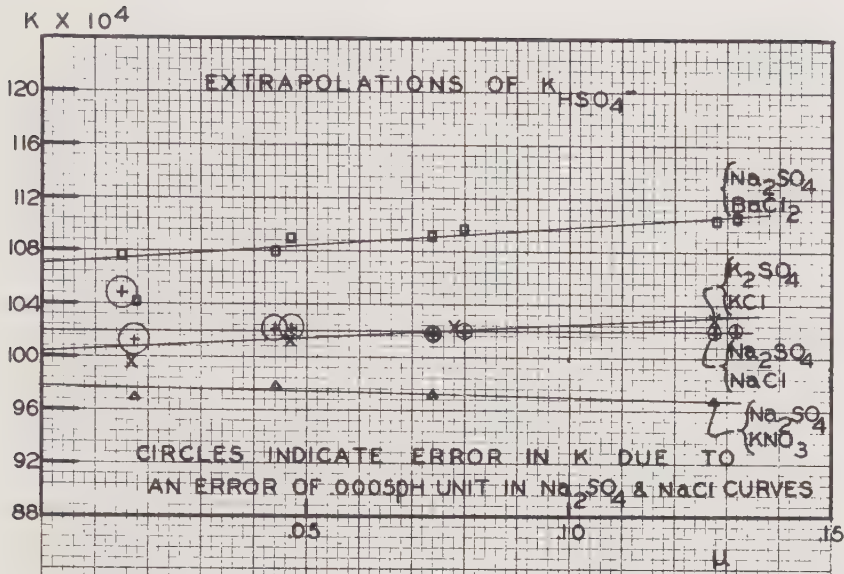


Figure 5

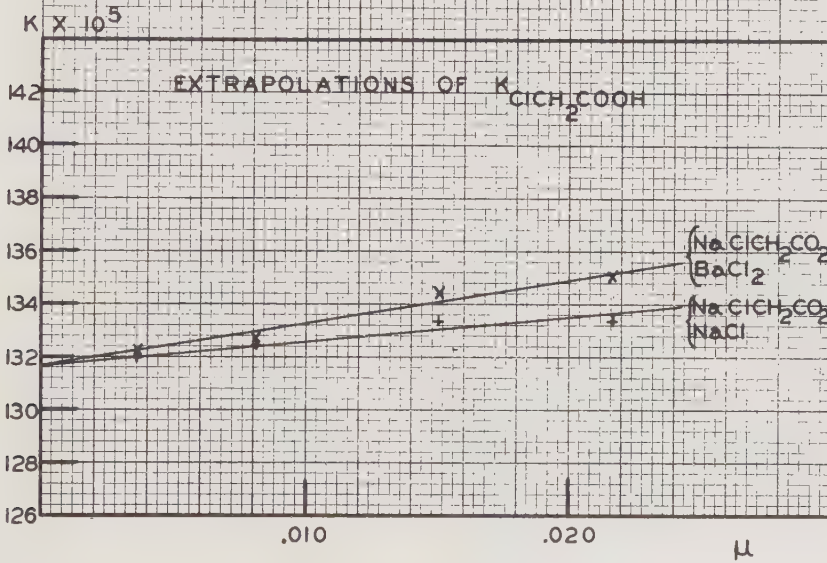


Figure 6

TABLE 3 - IONIZATION CONSTANT OF BISULFATE ION

Salt Pair, Temperature, Value of Parameter	μ	$\frac{(H^+)(SO_4^{2-})}{(HSO_4^-)}$	$\text{Log } \frac{\gamma_{H^+} \gamma_{SO_4^{2-}}}{\gamma_{HSO_4^-}} = \frac{-2.034 \sqrt{\mu}}{1 + a \sqrt{\mu}}$	K
Na_2SO_4	.00000			(.01020)
$NaCl$	.01567	.01682	-.2057	.01048
	.01747	.01658	-.2149	.01011
	.04426	.02058	-.3058	.01018
$t = 24.9^\circ C.$	.04735	.02105	-.3131	.01024
	.07408	.02351	-.3649	.01015
$a = 1.9$	.07948	.02405	-.3734	.01018
	.12733	.02764	-.4325	.01021
	.13267	.02803	-.4378	.01023
Na_2SO_4	.00000			(.01072)
$BaCl_2$	.01570	.01728	-.2069	.01073
	.01747	.01715	-.2161	.01043
	.04429	.02195	-.3082	.01079
$t = 24.9^\circ C.$	.04738	.02261	-.3157	.01093
	.07411	.02553	-.3683	.01093
$a = 1.85$	.07951	.02614	-.3769	.01097
	.12736	.03020	-.4372	.01104
	.13273	.03064	-.4427	.01106
Na_2SO_4	.00000			(.00978)
KNO_3	.01747	.01582	-.2127	.00969
	.04429	.01957	-.3013	.00978
$t = 24.9^\circ C.$	.07411	.02218	-.3585	.00972
$a = 2.0$	.12733	.02559	-.4235	.00965
K_2SO_4	.00000			(.01006)
KCl	.01687	.01620	-.2118	.00995
	.04705	.02084	-.3123	.01015
$t = 24.8^\circ C.$	.07825	.02402	-.3713	.01022
$a = 1.9$	.12787	.02778	-.4329	.01025

TABLE 4 - IONIZATION CONSTANT OF CHLOROACETIC ACID

Salt Pair, Temperature	μ	$\frac{(H^+)(A^-)}{(HA)}$	$\text{Log } \frac{\gamma_{H^+} \gamma_{A^-}}{\gamma_{HA}} = \frac{-1.017 \sqrt{\mu}}{1 + 2.0 \sqrt{\mu}}$	K
NaA	.00000			(.001316)
$NaCl$	.00358	.001496	-.0543	.001320
	.00814	.001584	-.0777	.001325
	.01501	.001683	-.1001	.001337
$t = 24.8^\circ C.$	.02174	.001742	-.1158	.001334
NaA	.00000			(.001316)
$BaCl_2$	.00358	.001498	-.0543	.001322
	.00814	.001587	-.0777	.001327
	.01501	.001693	-.1001	.001345
$t = 24.8^\circ C.$	.02174	.001762	-.1158	.001350

be based upon consideration of the following errors.

1. Error due to effect of temperature on the ionization constant of the indicator.--The ionization constant of methyl orange changes about 4% per degree.¹ This corresponds to a change of about 0.2% for 0.05 of a degree, and would have the same effect on our calculations as if the hydrogen ion concentration had changed by 0.2%. Such a change in hydrogen ion concentration in turn is equivalent to a change of 0.001 in $\log(H^+)$. In actual practice, however, any one spot in the thermostat was usually constant to better than $\pm 0.05^\circ\text{C}$. Furthermore, the temperature of the solutions would change more slowly and therefore less than that of the air. Finally, since both the reference cell and working cell would change in the same direction the actual error due to fluctuations in temperature would be less than 0.001 pH unit.

2. Error due to volume changes occurring in salt additions.--Rough experiments were carried out to determine the volume changes caused by the addition of the maximum amount of salt. The largest volume changes found were 0.2% (for NaCl). This can be shown to correspond to an error of 0.001 pH unit for the largest amount of salt added, less for smaller amounts. Even if the error were larger it would probably be eliminated by the extrapolation procedure in the final calculations of $K_{\text{HSO}_4^-}$.

3. Error due to change in hydrogen ion concentration due to ionization of indicator.--The equilibrium of the indicator may be represented by



The total concentration of indicator was usually about 3×10^{-6} mole/liter. Since the hydrogen ion concentration was usually adjusted to a value such that $(\text{I}^-)/(^+\text{HI}^-)$ was about 1.0, the concentration of $(^+\text{HI}^-)$ before the addition of salt was about 1.5×10^{-6} mole/liter. Upon the addition of neutral salt $(\text{I}^-)/(^+\text{HI}^-)$ changed to about 1.3 so that the final concentration of $(^+\text{HI}^-)$ was about 1.3×10^{-6} mole/liter. The increase in hydrogen ion concentration was therefore 0.2×10^{-6} mole/liter or in a total hydrogen ion concentration of about 4×10^{-4} a change of 0.05%, i.e., about 0.0002 pH unit. A similar analysis for Na_2SO_4 additions reveals a maximum error of about 0.0007 pH unit. The net error,

¹Tizard and Whiston, J. Chem. Soc., **117**, 150 (1920).

therefore, would be 0.0005 pH unit for the highest concentration of added salt, less for smaller concentrations.

4. Effect of dissolved CO₂.--The dissociation constant of H₂CO₃ is 4.31×10^{-7} at 25°C.¹ Substituting appropriate values for (H₂CO₃) and (H⁺), we obtain

$$(\text{HCO}_3^-) = 4.31 \times 10^{-7} \frac{1.2 \times 10^{-5}}{4 \times 10^{-4}} = 1.2 \times 10^{-8}$$

This amounts to an error of about 0.003% (0.00002 pH unit) in the hydrogen ion concentration.

5. The validity of Beer's Law for methyl orange.--G.Kortum² has investigated the validity of Beer's Law for the basic form of methyl orange for various wave lengths of incident light. Even with the extreme precision of his apparatus he has been able to detect only small deviations for visible light and these only at concentrations above 3×10^{-5} molar, a value almost ten times the concentration used in this research.

To make certain that the acid form of methyl orange also obeys Beer's Law, the light absorptions were determined for acid solutions of indicator from 3×10^{-7} to 3×10^{-6} mole/liter. No deviations from linearity were detected (see Table 5 and Figure 7).

TABLE 5 - VALIDITY OF BEER'S LAW FOR ACID FORM OF METHYL ORANGE

Gm./Liter	Mole/Liter*	Log(I _N /I) Observed	Log(I _N /I) Calculated*	Deviation
.000 x 10 ⁻⁴	0.00 x 10 ⁻⁷	.0159	.01636	-.00046
1.092	3.34	.0592	.05916	+.00004
3.247	9.93	.1440	.14360	+.00040
5.365	16.40	.2268	.22660	+.00020
7.43	22.68	.3077	.30752	+.00018
10.45	32.00	.4255	.42586	+.00036
				Mean+.00027

*Least Square Equation: $\text{Log}(I_N/I) = .01636 + .039186(\text{gm. 'liter})$.

6. Error due to decomposition of the indicator.--To investigate the possibility of decomposition of indicator a number of experiments were carried out at higher temperatures and with the illumination similar to that used in any actual set of measurements. These showed that at 55°C. the rate of decomposition

¹Shedlovsky and MacInnes, J. A. C. S., 57, 1705 (1935).

²Kortum, Zeit. f. Phys. Chem., B34, 255 (1936).

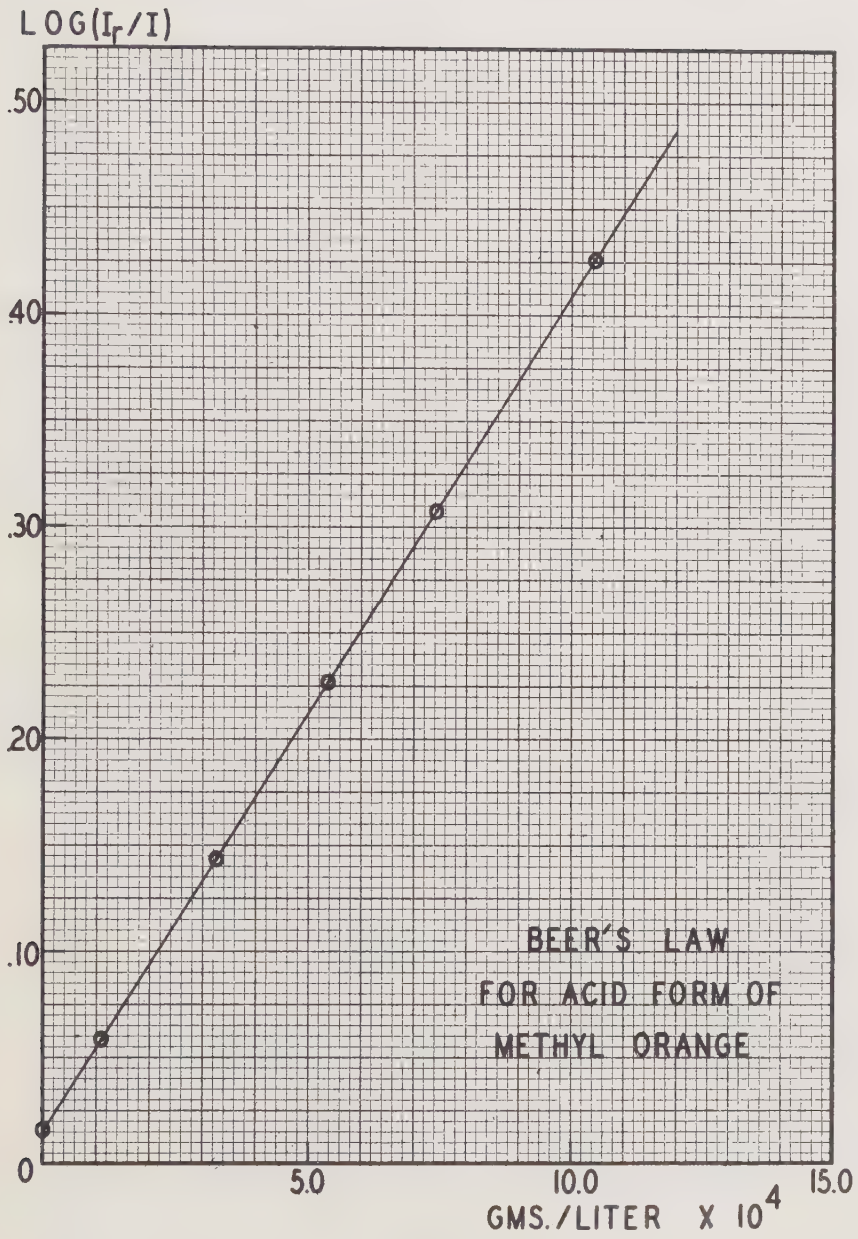


Figure 7

was extremely small, if it existed at all, and was the same in the presence of Na_2SO_4 or NaCl as in the absence of these salts. At 65°C . some decomposition of the indicator was detected, but in a period of an hour the amount of decomposition was just slightly beyond the possible experimental error.

B. Neutral Salt Effects on Methyl Orange

Although a number of laboratories¹ have investigated the behavior of methyl orange in the presence of various salts, most of the work has been carried out in buffer solutions and at concentrations above 0.5 molar. Only Sidgwick and his co-workers² have carried out investigations, and these for only one salt, NaCl , in which concentrations as low as 0.001 normal were used. Unfortunately, however, no provisions were made for controlling the temperature of the absorption cells; and since the ionization constant of methyl orange changes about 4% per degree,³ large errors may enter if the temperature of the cells depends directly upon the room temperature. Nevertheless, the general shapes and the position of the maxima of the curves obtained by Sidgwick, Worboys and Woodward agree fairly well with the data recorded in this thesis.

On Figure 4 one may readily observe that the neutral salt effect on methyl orange increases slightly with increasing temperature. The changes, however, are small compared to those found for Na_2SO_4 .⁴ The shapes of the curves also indicate an increase in the limiting slope in agreement with the Debye-Hückel theory. At 25°C . a least square equation through the NaCl data yields, upon differentiation, a limiting slope of -1.09, a value which is in satisfactory agreement with the theoretical one of -1.018. Since the method is capable of giving the limiting slope only within about 10%, it is impossible to make any quantitative com-

¹Güntelberg and Schiödt, Zeit. f. Phys. Chem., **135**, 393 (1928); Sidgwick, Worboys, and Woodward, Proc. Roy. Soc., **129**, 537 (1930); Thiel and Coch, Zeit. Anorg. Chem., **217**, 353 (1934).

²Sidgwick, Worboys, and Woodward, loc. cit.

³Tizard and Whiston, loc. cit.

⁴Singleterry, Ph. D. Dissertation, University of Chicago, 1940.

parison with the theoretical prediction of a 9% change between 5° and 55°C.

Figure 3 shows the dependence of the activity coefficient ratio for the indicator (see eq. (22) and (23)) upon the type of salt present. The chlorides have equal effects up to a concentration of about 0.01 molar even though the charge types are different. The effect of KNO_3 , however, shows a specific difference at much lower concentrations.

C. The Precision of the Ionization Constants Obtained

The influence of specific ion effects upon the precision of the determination of the ionization constant of an acid depends primarily upon the magnitude of that constant. For chloroacetic acid, with a constant of about 10^{-3} , the difference between the two values of the constant obtained when NaCl and BaCl_2 are used as the neutral salts is entirely negligible and not detectable on even a large scale plot (see Figure 6). On the other hand for HSO_4^- , whose ionization constant at 25°C. is near 10^{-2} , the constant obtained with BaCl_2 as the neutral salt is almost 6% higher than that obtained with NaCl (see Figure 5). With increasing temperature, however, this discrepancy decreases¹ until at 55°C. the two values agree within experimental error; the BaCl_2 value is about 0.7% below the NaCl one. Even at 25°C. however, the values of $K_{\text{HSO}_4^-}$ obtained by pairing Na_2SO_4 and NaCl , and K_2SO_4 and KCl are within 1.0% of each other; and no other pairings give constants more than 6% away from the Na_2SO_4 - NaCl one.

It is quite likely that these large differences due to specific ion effects would be reduced appreciably if an indicator showing smaller specific salt effects were used. Work by J. Mullane² indicates that bromcresol green is such an indicator. Unfortunately the magnitude of the salt effects on bromcresol green are almost three times as large as those for methyl orange. Nevertheless, this sulfonphthalein indicator may prove to be even better than methyl orange for the determination of ionization constants near 10^{-2} .

Small circles have been drawn around the individual points

¹Singleterry, loc. cit.

²Mullane, loc. cit.

of one curve to illustrate the effect on $K_{\text{HSO}_4^-}$ of an error of 0.001 unit in $\Delta \log (H^+)$. Such errors, however, would be overshadowed by the uncertainty due to specific ion effects.

CONCLUSION

A method has been developed which makes it possible to obtain ionization constants near 10^{-2} with a maximum uncertainty of about 6%, and an absolute error probably not greater than 2%. The precision of the method rises rapidly as K decreases to 10^{-3} or less, and the method is readily applicable to most types of acid-base equilibria. For equilibria involving divalent ions, the method is the most precise one available, and has been utilized by C. R. Singleterry¹ for the determination of the heat of ionization of bisulfate ion. Since the ionization constants of HSO_4^- decrease rapidly with increasing temperature, the uncertainty in the K 's is much less than 6%. Hence a very precise value of ΔH° has been obtained.

¹Singleterry, loc. cit.

